ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 12, pp. 2793–2800. © Pleiades Publishing, Ltd., 2015.
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Synthesis and Crystal Structure of Thiolate-Bridged Dinuclear Platinum(II) Complexes

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Received May 29, 2015

Abstract—Reactions of 2,2′-bipyridine platinum(II) complexes with 2-aminoethanethiol or 2,2′-disulfanediyldi(ethan-1-amine) afforded new complexes $[Pt_2(\mu\text{-aet})(\mu\text{-aetH}^+)(bpy)_2](NO_3)_4\cdot 2H_2O$ and $[Pt_2(\mu\text{-aet})(\mu\text{-aetH}^+)\cdot(bpy)_2](NO_3)_4\cdot 5H_2O$ and heteronuclear complex *catena*-$[(bpy)Pt(\mu\text{-aet})Ag](NO_3)_2\cdot 3H_2O$ (bpy = 2,2′-bipyridine, aet = 2-aminoethanethiol). All complexes were characterized by elemental analyses and X-ray diffraction data.

Keywords: platinum, dinuclear complexes, thiolate complexes, crystal structure, 2-aminoethanethiol

DOI: 10.1134/S1070363215120221

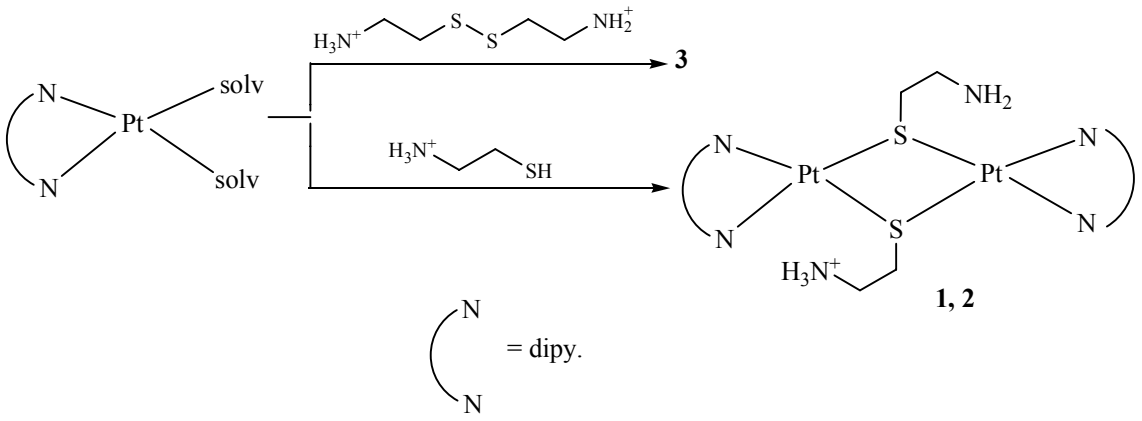
In recent time much attention has been focused on reactions of platinum and other *d*-element compounds with thiols, thioamino acids, and biologically active sulfur-containing endogenous compounds. The results of these studies are necessary to understand inactivation of antitumor platinum-containing cytotoxic drugs *in vivo* [1–5], as well as to design model catalysts responsible for the thiol–disulfide status in the human organism [6–8], imbalance of which [8] could lead to acute and (or) chronic disorders [9, 10].

It is known that redox regulation of cellular processes is mediated by thiol groups of cysteine [7] constituting structural units of proteins and some oligopeptides. Among these, a particular role is played by glutathione (GSH, L-γ-glutamyl-L-cysteinylglycine), is endogenous peptide present in all mammalian cells in considerable concentrations and functioning as regulator [7, 11]. Disturbance of the thiol–disulfide balance, i.e., of the ratio of the oxidized (disulfide, –S–S–) and reduced (thiol, –SH) cysteine residues ($2GSH + Ox \leftrightarrow GSSG + 2H^+$, where Ox is an oxidant represented by active oxygen species), may result in oxidative stress [12]. Reversible reduction of disulfide bonds to thiol groups *in vivo* is controlled by a number of enzymes, including metal-containing ones [7, 9, 10], whose active sites can be simulated by coordination compounds of *d* elements. On the basis of such compounds, pharmaceutical agents capable of regulating the thiol–disulfide status and thus modulating immune response of the organism as a whole have been developed [13–15].

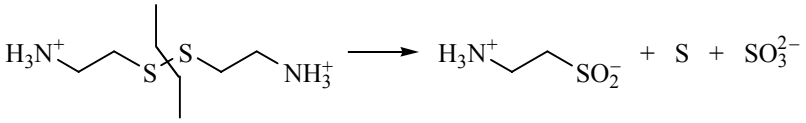
In keeping with the hard and soft acids and bases principle [16], thiols are soft bases that form strongest bonds in reactions with such soft Lewis acids as Pt(II) and Pd(II); thiols often behave as bridging ligands in complexes with Pt(II) and Pd(II) [17]. Information of the structure of biologically important thiol-containing complexes of *d*-elements may be interesting from the viewpoint of determining possible mechanisms of oxidation of thiol groups in thioamino acids, i.e., most of probable reaction paths and intermediate products.

Herein we report the results of studying the reaction of 2,2′-bipyridine platinum(II) complexes with 2-aminoethanethiol (aet) and its oxidized form, cystamine [cyst, 2,2′-disulfanediyldi(ethan-1-amine)]. We isolated and determined crystal structures of the following thiolate platinum complexes: $[Pt_2(\mu\text{-aet})\cdot(\mu\text{-aetH}^+)(bpy)_2](NO_3)_4\cdot 2H_2O$ (**1**), $[Pt_2(\mu\text{-aet})(\mu\text{-aetH}^+)\cdot(bpy)_2](NO_3)_4\cdot 5H_2O$ (**2**), and *catena*-$[(bpy)Pt(\mu\text{-aet})\cdot Ag](NO_3)_2\cdot 3H_2O$ (**3**). Complexes **1**–**3** were synthesized by reaction of $(bpy)PtCl_2$ with 2-aminoethanethiol or cystamine. (2,2′-Bipyridine)dichloroplatinum(II) $(bpy)PtCl_2$ was preliminarily converted into aquated species $(bpy)Pt(solv)_2$ (solv = H_2O, OH^-) [18] via reaction with silver nitrate at pH = 3 (Scheme 1).

Scheme 1.



Scheme 2.



It should be noted that reactions of diammine Pt(II) or Pd(II) with disulfides involving cleavage of the disulfide bond can lead to oligonuclear complexes. For example, *cis*-$[Pd(NH_3)_2Cl_2]$ reacted with cystamine to afford 18-nuclear complex $[Pd_{18}(\mu_3\text{-}S)_2(\mu\text{-aet})_{15}\cdot(\mu\text{-}SO_2(CH_2)_2NH_2)_3](NO_3)_7(SO_3)\cdot 0.5H_2O$; the reaction was accompanied by removal of ammonia molecules from the coordination sphere and partial oxidation of 2-aminoethanethiol [19]. Analogous reactions of cystamine with $[Pd(tmen)Cl_2]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in acid medium [19] (Scheme 2) and with palladium(II) chloride in aqueous ammonia [20] lead to hexanuclear thiolate-bridged paddle-wheel complexes $[Pd_2\{Pd(aet)_2\}_4]^{4+}$. As in the preceding case, the ammine ligands were removed completely from the inner coordination sphere, presumably due to strong *trans*-effect of the thiol [21]. In contrast, palladium(II) complexes with diamines exerting a strong *trans*-effect, e.g., with aromatic nitrogen containing heterocycles (pyridine, 2,2′-bipyridine, or 1,10-phenanthroline), reacted with both 2-aminoethanethiol and cystamine with retention of the ammine ligand, and the products were dinuclear thiolate-bridged complexes such as $[Pd_2(\mu\text{-aetH})_2\cdot(phen)_2](NO_3)_4\cdot H_2O$ [22] and $[Pd_2(\mu\text{-Cys})(\mu\text{-CysH})\cdot(bpy)_2](NO_3)_3\cdot 4.5H_2O$ [23].

Complexes **1** and **2** are poorly soluble in water and acetonitrile and almost insoluble in methanol, ethanol, acetone, and diethyl ether. Complex **3** is soluble in water and poorly soluble in acetonitrile, acetone, and diethyl ether, and it is readily reduced to the metal with lower alcohols. The crystallographic and structure refinement parameters of complexes **1**–**3** are given in Table 1.

The platinum atoms in complexes **1** and **2** have distorted square-planar environment formed by two nitrogen atoms of 2,2′-bipyridine and two sulfur atoms of the bridging 2-aminoethanethiolate ligand (Fig. 1). The average Pt–S bond lengths in **1** and **2** are equal to ~2.3 Å (Table 2), which is consistent with the data for structurally related complexes containing both aliphatic [24] and aromatic [25, 26] ammine ligands. The average Pt–N bond length in **1** and **2** (~2.03 Å) approaches that in platinum complexes with aromatic amines [25–28]. The Pt–N bond in platinum complexes with aliphatic amines (in the *trans* position with respect to thiolate ligand) is longer (2.3–2.4 Å) [24] due to stronger *trans*-effect of thiols, which is comparable to the *trans*-effect of aromatic amines [21]. This may favor removal of the amine ligand from the metal coordination sphere [19].

According to Connick et al. [29], dinuclear complexes can be stabilized by weak M···M interactions through overlap of the occupied $4d_z^2$ and vacant $5p_z$ orbitals of the neighboring metal atoms provided that the distance between these atoms is shorter than 3.5 Å (the Pt···Pt distance in complexes **1** and **2** is 3.009 and 3.032 Å, respectively). Short Pt···Pt distance in a particular dinuclear fragment favors excitation

Table 1. Crystallographic data and refinement parameters of complexes **1**–**3**

Parameter	**1**	**2**	**3**
Formula	$C_{24}H_{34}N_{10}O_{14}Pt_2S_2$	$C_{24}H_{40}N_{10}O_{17}Pt_2S_2$	$C_{24}H_{42}Ag_2N_{10}O_{19}Pt_2S_2$
Molecular weight	1140.91	1194.96	1444.72
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*1	*P*1	$P2_1/n$
a, Å	11.9220(10)	11.2773(2)	7.3079(9)
b, Å	12.0394(10)	12.1716(6)	22.197(3)
c, Å	13.4167(11)	14.5554(6)	24.958(3)
α, deg	86.809(2)	73.853(4)	90.00
β, deg	74.391(2)	82.523(3)	95.807(2)
γ, deg	65.046(2)	73.068(3)	90.00
V, Å^3	1677.9(2)	1833.28(12)	4027.8(8)
Z	2	2	4
d_{calc}, g/cm^3	2.258	2.165	2.382
F(000)	1096	1156	2760
μ, mm^{-1}	8.536	7.824	8.074
Reflection indices	$-16 \le h \le 16$ $-16 \le k \le 16$ $-15 \le l \le 18$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-18 \le l \le 18$	$-3 \le h \le 11$ $-29 \le k \le 33$ $-37 \le l \le 35$
$2\theta_{max}$, deg	30.00	27.50	32.50
Total/independent reflection number	9478/8721	8404/6776	14240/10695
R_{int}	0.0647	0.0348	0.1427
Number of variables	477	536	562
$\Delta\rho_{max}$, $\Delta\rho_{min}$, $\bar{e}$/Å^3	–3.717, 3.670	–1.118, 1.378	–3.294, 2.944
Goodness of fit	1.040	1.030	0.988
R Factors [reflections with $I > 2\sigma(I)$]:			
R_1	0.0292	0.0262	0.0433
wR_2	0.0763	0.0526	0.0956
R Factors (all reflections):			
R_1	0.0315	0.0405	0.0614
wR_2	0.0773	0.0573	0.1030

involving removal of an electron from the $d\sigma^*(4d_z^2)$ orbital of Pt···Pt to the bonding $p\sigma(5p_z)$ orbital; so that the order of the metal–metal bond can be formally regarded as increasing from 0 to 1/2 [29].

On the whole, the molecular structures of complexes **1** and **2** are similar (Fig. 1), and the bond lengths and bond angles therein coincide within 1% (Table 2). On the other hand, their crystal structures are essentially different. According to the X-ray diffraction data, unit cells of **1** and **2** contain two dinuclear cations $[Pt_2(\mu\text{-aet})(\mu\text{-aetH}^+)(bpy)_2]^{4+}$. The number of solvate water molecules influences arrangement of platinum atoms in the complexes, as well as non-covalent π–π-stacking interactions [30] between the aromatic bipyridine fragments. The interplanar distance between the bipyridine ligands of the neighboring dinuclear cations $[Pt_2(\mu\text{-S-aet})(\mu\text{-S-aetH}^+)\cdot(bpy)_2]^{4+}$ is ~3.2174 and ~3.2416 Å in crystalline complexes **1** and **2**, respectively. The distances between the neighboring cation dimers of complexes **1** and **2** also differ insignificantly, ~3.383 and 3.016 Å, respectively (Fig. 2).

The bridging 2-aminoethanethiolate ligands are arranged *cis* with respect to the $[Pt_2(\mu\text{-aet})(\mu\text{-aetH}^+)\cdot$

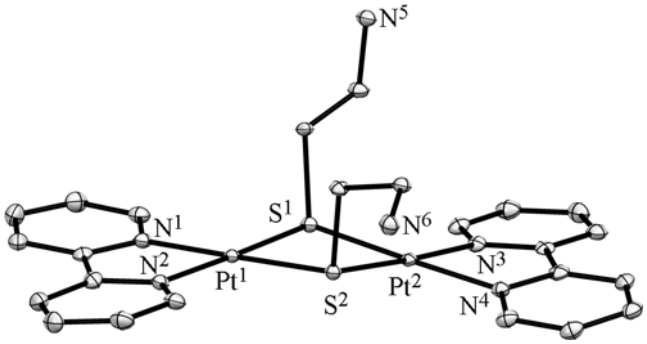


Fig. 1. Structure of the $[Pt_2(\mu\text{-aet})(\mu\text{-aetH}^+)(bpy)_2]^{4+}$ cation in complexes **1** and **2** according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%; hydrogen atoms are not shown.

$(dipy)_2]^{4+}$ dinuclear cation plane (Fig. 1). This structure allows the cations to form dimers through π–π stacking between the bipyridine ligands (Fig. 2), and the dimers in turn give rise to 2D layers stabilized by a hydrogen bond system involving the amino nitrogen atoms of the thiolate ligands, crystallization water molecules, and nitrate ions.

The platinum atoms in complex **3** have distorted square–planar configuration. The coordination entity is formed by two nitrogen atoms of the bipyridine ligand and nitrogen and sulfur atoms of the thiolate ligand (Fig. 3). 2-Aminoethanthiolate in complex **3** is a tetradentate μ_3-bridging ligand chelating platinum atom. The average $Pt–N_{bpy}$ distance (~2.03 Å, Table 3) is consistent with the data for structurally related complexes [25–28]. It is interesting that the $Pt–N_{aet}$ bond is short (2.04 Å), which is more typical of aromatic ammine ligands. Presumably, complex **3** is formed according to a scheme similar to that proposed in [31, 32] for the reactions of chelate Pd(II), Ni(II), and Co(II) complexes with 2-aminoethanethiol and Au^+, Ag^+, Pd^{2+}, or Ni^{2+} salts (Scheme 3).

Complex **3** consists of (bpy-κ^2*N*,*N*′)Pt(aet-κ*S*,κ*N*) fragments linked by bridging silver atoms to a continuous one-dimensional chain stabilized by π–π stacking between bipyridine ligands of the neighboring fragments and bridging nitrate ligands (Fig. 3). The average distance between the neighboring bipyridine fragments is 3.44 or 3.46 Å (Fig. 3). The distance between the platinum atoms of the neighboring fragments is fairly long (~5.1 Å), which hardly allows stabilization of the 1D chain through metal–metal interaction [29].

Thus, the (bpy-κ^2*N*,*N*′)Pt(aet-κ*S*,κ*N*) units of complex **3** are linked to infinite 1D structure through silver atoms that are coordinated to the thiolate's sulfur atoms and additionally bridged by nitrate ions. The silver atoms occur in distorted tetrahedral or tetragonal–pyramidal coordination environment composed of sulfur atoms of the 2-aminoethanethiolate ligands and oxygen atoms of bridging and chelating nitrate ions (Fig. 3). The average $Ag–O(NO_3^-)$ bond length is 2.53 Å (2.42–2.67 Å, Table 3), which is typical of structurally related compounds [33]. Bridging nitrate

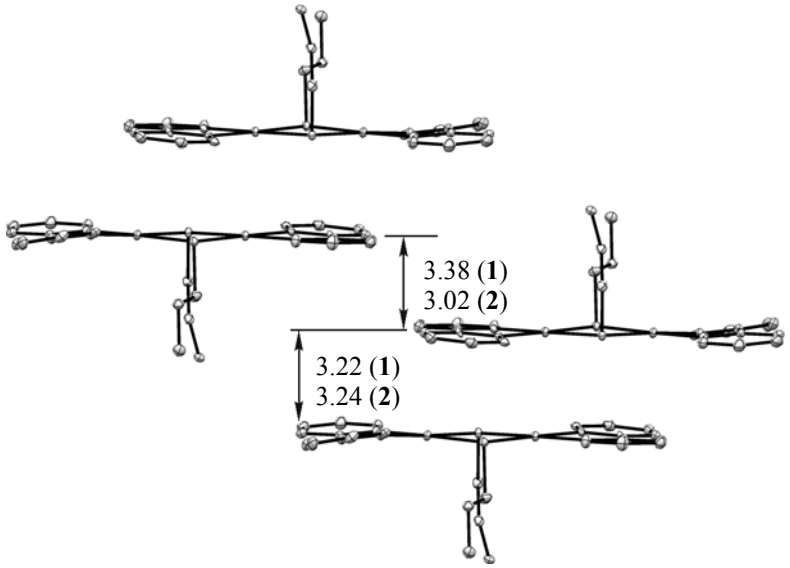


Fig. 2. Crystal packing of complexes **1** and **2**; π–π stacking interactions (Å) between the bypiridine ligands in the dimers and between the neighboring dimers are shown; nitrate ions, crystallization water molecules, and hydrogen atoms are omitted.

Table 2. Principal bond lengths and bond angles in molecules **1** and **2**

Bond	*d*, Å	Angle	τ, deg
$Pt^1–N^1$	2.028 (1)	$N^1Pt^1N^2$	80.46 (1)
	2.047 (2)		80.10 (2)
$Pt^1–N^2$	2.044 (1)	$S^1Pt^1S^2$	82.04 (1)
	2.034 (2)		82.41 (2)
$Pt^1–S^1$	2.288 (1)	$N^3Pt^2N^4$	80.23 (1)
	2.304 (2)		80.73 (2)
$Pt^1–S^2$	2.298 (1)	$S^1Pt^2S^2$	81.89 (1)
	2.299 (2)		82.53 (2)
$Pt^2–N^3$	2.044 (1)	$Pt^1S^1Pt^2$	97.70 (1)
	2.041 (2)		97.20 (2)
$Pt^2–N^4$	2.053 (1)	$Pt^1S^2Pt^2$	96.68 (1)
	2.042 (2)		97.74 (2)
$Pt^2–S^1$	2.283 (1)		
	2.306 (2)		
$Pt^2–S^2$	2.309 (1)		
	2.306 (2)		

Table 3. Principal bond lengths and bond angles in molecule **3**

Bond	*d*, Å	Bond	*d*, Å	Angle	τ, deg
$Pt^2–N^1$	2.032	$Ag^2–S^1$	2.456	$N^1Pt^2N^2$	80.47
$Pt^2–N^2$	2.026	$Ag^1–S^1$	2.459	$S^2Pt^2N^3$	84.74
$Pt^2–N^3$	2.041	$Ag^1–S^2$	2.451	$N^4Pt^1N^5$	79.92
$Pt^2–S^2$	2.275	$Ag^2–S^2$	2.557	$N^6Pt^1S^1$	84.75
$Pt^1–N^4$	2.029	$Ag^2–O^1$	2.419	$S^2Ag^2S^1$	122.99
$Pt^1–N^5$	2.026	$Ag^2–O^6$	2.459	$Ag^2S^1Ag^1$	94.46
$Pt^1–N^6$	2.060	$Ag^1–O^5$	2.605	$S^1Ag^1S^2$	135.33
$Pt^1–S^1$	2.270	$Ag^1–O^1$	2.672	$Ag^1S^2Ag^2$	99.42
		$Ag^1–O^2$	2.521		
		$Ag^2–O^1$	2.419		

ligands link two infinite 1D chains to each other, thus forming a stair motif (Fig. 4). Free Ag^+ ions were not detected in freshly prepared solutions of **3**, which indicates high strength of the complex and the existence of large oligonuclear fragments in solution.

EXPERIMENTAL

The IR spectra (5000–400 cm^{-1}) were recorded in KBr on an FSM-1202 spectrometer (Infraspek) with Fourier transform. The elemental analyses for carbon, nitrogen, and sulfur were obtained on a LECO CHNS(O)-932 analyzer. The metal content was determined by reduction of samples in a stream of dry hydrogen at 600–700°C and weighting.

The X-ray diffraction data for single crystals of complexes **1**–**3** were obtained on a Bruker Smart APEX II diffractometer equipped with a two-dimensional CCD detector (MoK_α radiation, λ = 0.71073 Å; graphite monochromator) at the "Research Center for X-Ray Diffraction Studies" resource center of the St. Petersburg State University. The structures were solved directly and were refined by the full-matrix least-squares procedure in anisotropic approximation for all non-hydrogen atoms using SHELXL software package [34]. The positions of hydrogen atoms in organic fragments were calculated by SHELX algorithms. The positions of hydrogen atoms in water molecules were determined from the Fourier difference maps and were fixed for the refinement procedure. The X-ray diffraction data for complexes **1**–**3** were deposited to the Cambridge Crystallographic Data Centre [CCDC entry nos. 1055492 (**1**), 1055491 (**2**), and 1055493 (**3**)].

(2,2′-Bipyridine)dichloroplatinum(II) [Pt(dipy)Cl_2] was synthesized as described in [6]. Commercial 2-

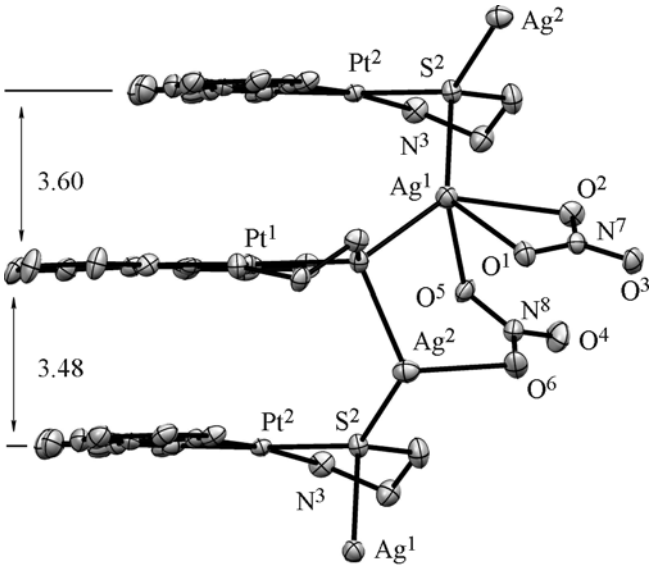
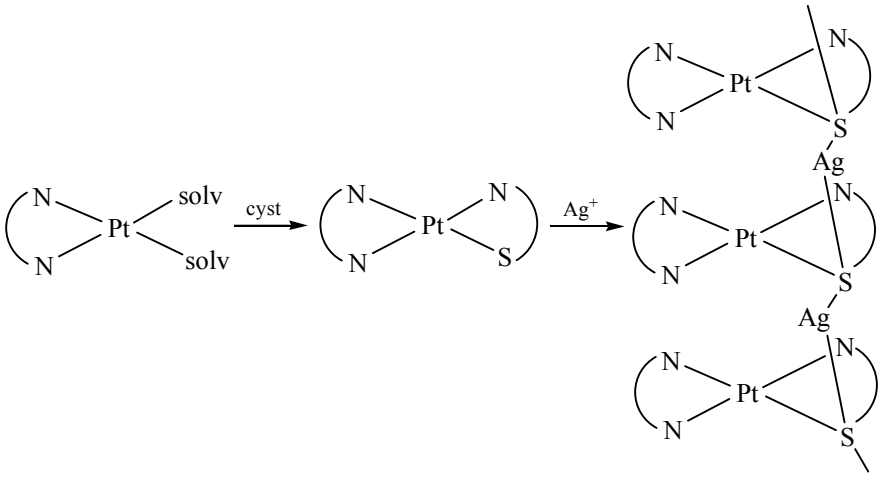


Fig. 3. A fragment of the molecular structure of complex **3** according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibrations ellipsoids with a probability of 50%. π–π Stacking interactions (Å) between the bipyridine ligands and coordination modes of nitrate ions are shown.

Scheme 3.



aminoethanethiol hydrochloride (chemically pure grade, *Vekton*), 2,2′-disulfanediyldi(ethanamine) (analytical grade), silver nitrate (chemically pure grade), and 2,2′-bipyridine (analytical grade) (*Neva Reaktiv*) were used without additional purification.

Di-μ-(2-aminoethanthiolato)bis[(2,2′-bipyridine) platinum(II)] tetranitrate dihydrate (1) and pentahydrate (2). A solution of 206.4 mg (1.215 mmol) of silver nitrate in 5 mL of water was added to a suspension of 171.0 mg (0.405 mmol) of $[Pt(bpy)Cl_2]$

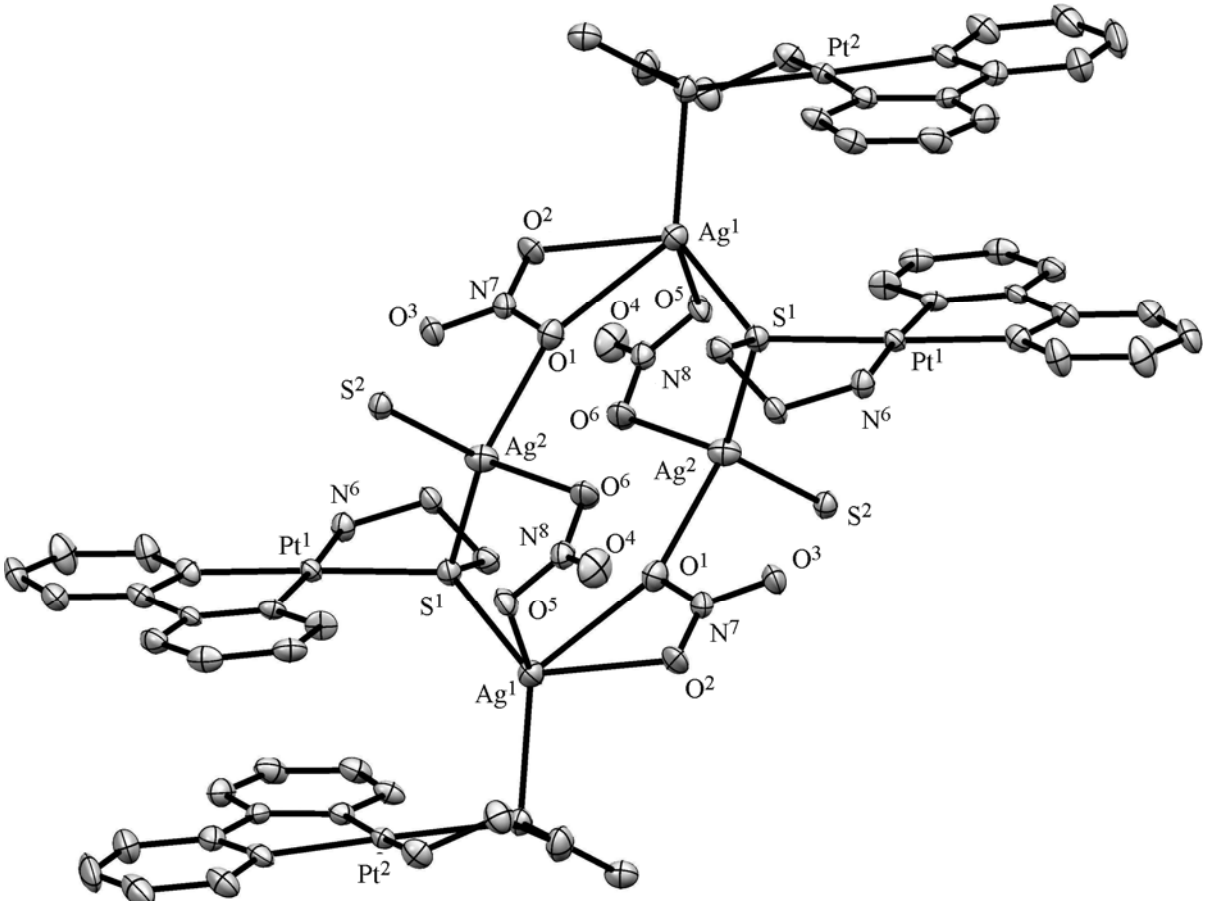


Fig. 4. Crystal packing of complex **3** represented as thermal vibration ellipsoids with a probability of 50%. Solvate water molecules and hydrogen atoms are not shown.

in 10 mL of water. The mixture was acidified with 0.5 M nitric acid to pH 3 and heated for 4–5 h at 70°C. The precipitate of silver nitrate was filtered off, a solution of 46.0 mg (0.405 mmol) of 2-aminoethanethiol hydrochloride in 5 mL of water was added to the filtrate, and the mixture was heated for 1 h at 70°C. The yellowish flaky solid was filtered off, the filtrate was evaporated on a rotary evaporator to a volume of 5–7 mL, and the residue was left to stand on exposure to air for crystallization of complex **1**. Complex **2** crystallized on slow evaporation. Complex **1**: yield ~70%. Found, %: C 25.26; H 2.92; N 12.20; Pt 34.20; S 5.61. $C_{24}H_{34}N_{10}O_{14}S_2Pt_2$. Calculated, %: C 25.27; H 3.00; N 12.28; Pt 34.20; S 5.62. Complex **2**: yield ~70%. Found, %: C 24.11; H 3.30; N 11.74; Pt 32.65; S 5.36. $C_{24}H_{40}N_{10}O_{17}S_2Pt_2$. Calculated, %: C 24.12; H 3.37; N 11.72; Pt 32.65; S 5.37.

Complex (3). A solution of 323.4 mg (1.904 mmol) of silver nitrate in a minimum volume of water was added to a suspension of 201 mg (0.476 mmol) of $[Pt(bpy)Cl_2]$ in 10 mL of water. The mixture was acidified with dilute (0.5 M) nitric acid to pH 3 and heated for 4–5 h at 70°C. The precipitate of silver chloride was filtered off, a solution of 54 mg (0.238 mmol) of cystamine in 10 mL of water was added to the filtrate, and the mixture was heated for 1 h at 70°C. The white flaky solid was filtered off, and the filtrate was evaporated to a volume of 5–7 mL and left to stand for crystallization to obtain crystals suitable for X-ray analysis. Yield 40%. IR spectrum, ν, cm^{-1}: 3500 w.br, 3428 w.br, 3123 m, 3078 m, 3052 m, 3041 m, 1610 s, 1472 m, 1452 m, 1384 v.s, 1370 v.s, 1319 v.s, 1161 m, 774 m, 721 m.

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